Electronic decoherence time for non-Born-Oppenheimer trajectories

Ahren W. Jasper and Donald G. Truhlar[a)]

Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431

An expression is obtained for the electronic decoherence time of the reduced density electronic matrix in mixed quantum-classical molecular-dynamics simulations. The result is obtained by assuming that decoherence is dominated by the time dependence of the overlap of minimum-uncertainty packets and then maximizing the rate with respect to the parameters of the wave packets. The expression for the decay time involves quantities readily available in non-Born-Oppenheimer molecular-dynamics simulations, and it is shown to have a reasonable form when compared with two other formulas for the decay time that have been previously proposed. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1995695]

I. INTRODUCTION

The time-dependent Schrödinger equation describes the unitary evolution of a pure state, such as the wave function of the entire universe. Real systems interact with an environment and are described by a reduced density matrix for the system's degrees of freedom, traced over the environment. A reduced density matrix evolves nonunitarily under the influence of friction and dissipation, and, in an appropriate basis, its off-diagonal elements, called coherences, decay to zero; this is called decoherence. The decoherence rate depends strongly on the initial conditions and it can be fast—on the other of the highest natural frequency of the system.[1] The environment that produces decoherence also produces a back reaction on the system, modifying its evolution.[2] The basis in which decoherence is fastest is called the pointer basis.[3] The density matrix, being Hermitian, may be diagonalized at any time, but the basis that diagonalizes it changes with time. After decoherence, though, the density matrix remains diagonal in the pointer basis for a given environment.[4,5]

Although considerable literature has been developed for decoherence in the limit of weak system-environment coupling, chemical physics is replete with problems where decoherence must be understood in the limit of strong system-bath coupling; electron transfer reactions and exciton transfer in condensed phases provide two prominent examples.[6–8] Electron transport in molecule-based electronics[9,10] also involves questions of localization and dissipation that would naturally be treated by reduced density matrices. There are many qualitatively different models that one could use for the environment of the system. The most frequently studied one is a collection of harmonic oscillators, but recent work has begun to consider other kinds of baths such as a gas reservoir of variable density.[11] The present article considers decoherence in yet another kind of system, namely, the electronic degrees of freedom of a molecule coupled to an environment of nuclear degrees of freedom, which must be understood to develop physical models of electronically nonadiabatic processes. The question is how rapidly the electronic density matrix decoheres due to vibrational motion.

Rossky and co-workers[12,13] analyzed the problem by considering the behavior of Gaussian wave packets. Their treatment attributes the decay of coherences to decaying overlap of wave packets centered on diverging nuclear trajectories corresponding to propagation in the different electronic states. The overlap is evaluated under the assumption that the initial momenta of trajectories in different states are the same, which is a special case corresponding to initially degenerate states; the coordinate dispersion of the wave packet was based on a simple realistic model of a thermal environment, and the momentum dispersion of the wave packet was implicit (for a given coordinate dispersion) in the assumed form of the frozen Gaussian wave packet. The leading term in the decay of the overlap is second order in the time. This stimulating treatment raises questions about whether one can better justify the form and width assumed for the wave packet, whether one can identify a first-order contribution to the decay, and whether one can extend the result to nonthermal environments.

In our own work, we have developed an alternative approach,[14–16] based on the fastest natural time scale of the system and the need, in a self-consistent treatment including back reaction, for decoherence to slow down (and eventually stop) as the nuclear momenta are decreased (eventually to zero). Although it has been successful in applications, this approach is also not completely satisfactory because it contains parameters whose order of magnitude may be estimated with reasonable confidence, but which are otherwise arbitrary.

There is some encouraging consistency between the two approaches. In particular the fastest-time-scale approach[14–16] gives very fast decoherence times ($2-34$ fs) even for gas-phase molecules. The Gaussian wave-packet approach, originally developed for condensed-phase systems,[12] has now been analyzed in terms of intramolecular and intermolecular contributions, and it has been found that it also gives fast times[13,17] (~ 4 fs) for decoherence due to intramolecular mo-

a)Electronic mail: truhlar@umn.edu

tion, such that intramolecular motions can have a much greater effect on the electronic decoherence than polar solvent molecules do.

In the present article we return to the derivation on the basis of wave packets, and we use the principles developed[3] on the basis of environment-induced superselection rules to remove some of the arbitrariness in the choice of wave-packet widths. The principles employed are the following:[3]

(1) The semiclassical limit of a wave function is a sum of WKB-type trajectories associated with minimum uncertainty wave packets, and the decoherence of the superposition is faster than the decoherence of the individual packets.
(2) The pointer basis is the one in which decoherence is fastest.

Section II presents and discusses the theory and Sec. III summarizes the conclusions.

II. THEORY

Semiclassical analyses based on perturbation theory[18] and on the short-time behavior of wave packets[12,13] have shown that the decoherence of the reduced electronic density matrix may be associated with two effects: pure dephasing (which refers to the loss of coherence due to interference among the phases associated with the various members of the ensemble of semiclassical trajectories) and decoherence due to the divergence of the trajectories. In this paper, we present an analysis of the behavior of the time dependence of decoherence in terms of the nuclear overlap in semiclassical trajectories.

The nuclear wave function χ_α for each electronic state α is taken to be a one-dimensional minimum-uncertainty wave packet,

$$\chi_\alpha = \frac{1}{(2\pi\sigma_\alpha^2)^{1/4}} \exp(-(x-x_\alpha)^2/4\sigma_\alpha^2)\exp(-ip_\alpha x/\hbar), \quad (1)$$

where x and p are the nuclear position and momentum and x_α, p_α, and σ_α are parameters. (At this point, we could factor out the phase at the center of the wave packet[13,19] to explicitly see its effect, but we will not do this.) Equation (1) has the properties $\langle x \rangle = x_\alpha$, $\langle p \rangle = p_\alpha$, $\Delta x = \sigma_\alpha$, and $\Delta x \Delta p = \hbar/2$, where brackets denote an expectation value and Δq is the uncertainty in q.

The overlap for two such packets in different electronic states α and β is

$$\langle \chi_\alpha | \chi_\beta \rangle = O_{\alpha\beta} = N_{\alpha\beta} \exp(-A_{\alpha\beta})\exp(-i\Phi_{\alpha\beta}). \quad (2)$$

where

$$N_{\alpha\beta} = \sqrt{\frac{2\sigma_\alpha\sigma_\beta}{\sigma_\alpha^2 + \sigma_\beta^2}}, \quad (3)$$

$$A_{\alpha\beta} = \frac{(x_\alpha - x_\beta)^2}{4(\sigma_\alpha^2 + \sigma_\beta^2)} + \frac{\sigma_\alpha^2\sigma_\beta^2}{\sigma_\alpha^2 + \sigma_\beta^2}\frac{(p_\alpha - p_\beta)^2}{\hbar^2}, \quad (4)$$

and

$$\Phi_{\alpha\beta} = \frac{\sigma_\alpha^2\sigma_\beta^2}{\sigma_\alpha^2 + \sigma_\beta^2}\frac{(p_\beta - p_\alpha)}{\hbar}\left(\frac{x_\alpha}{\sigma_\alpha^2} + \frac{x_\beta}{\sigma_\beta^2}\right). \quad (5)$$

Taking the time derivative of Eq. (2) and ignoring the time dependence of the widths σ_α and phase $\Phi_{\alpha\beta}$ gives

$$\dot{O}_{\alpha\beta} = -O_{\alpha\beta}\dot{A}_{\alpha\beta}, \quad (6)$$

i.e., $\dot{A}_{\alpha\beta}$ is the first-order decay rate constant $k_{\alpha\beta}$ for the decay of the nuclear overlap.

Since, in the semiclassical limit, the center of the Gaussian wave packet follows a classical trajectory,[19] we make the approximations $\dot{x}_\alpha = p_\alpha/m$ and $\dot{p}_\alpha = F_\alpha$, where m is the nuclear mass and F_α is the nuclear force. This yields

$$k_{\alpha\beta} = \frac{(x_\alpha - x_\beta)(p_\alpha - p_\beta)}{2m(\sigma_\alpha^2 + \sigma_\beta^2)} + \frac{2\sigma_\alpha^2\sigma_\beta^2(p_\alpha - p_\beta)(F_\alpha - F_\beta)}{(\sigma_\alpha^2 + \sigma_\beta^2)\hbar^2}. \quad (7)$$

The above analysis is similar to that of Rossky and co-workers.[12,13] In their analyses, however, they assume that $p_\alpha = p_\beta$ and $x_\alpha = x_\beta$, and they find no first-order decay.

Note that the nuclear momentum appears in Eq. (7) in two different contexts: (1) as a parameter defining the wave packets in Eq. (1) and (2) in the expression for the time dependence of the nuclear coordinate. In some limits (e.g., that of a quadratic potential where the wave packet follows a classical trajectory), these two meanings are equivalent, but in general they are not.

The time dependence of the widths may be an important aspect of decoherence. Qualitatively, including the time dependence of the widths would result in (1) another first-order decay term involving $\dot{N}_{\alpha\beta}$, and (2) additional terms in the expression for $\dot{A}_{\alpha\beta}$ involving $\dot{\sigma}_\alpha$. The first contribution may be safely neglected, noting that $N_{\alpha\beta} = 1$ in the limit where $\sigma_\alpha = \sigma_\beta$. The second contribution may be neglected if the effect of $\dot{x}_\alpha$ and $\dot{p}_\alpha$ on the decay rate is more significant than the effect of $\dot{\sigma}_\alpha$, which is reasonable and which is consistent with the first principle from the Introduction on which our derivation is based.

For single-surface semiclassical trajectory dynamics, the wave-packet parameters x_α and p_α may be chosen to correspond to the position and momentum of a classical trajectory. This correspondence is exact if the potential is truncated at second order.[19] An expression for the time dependence of the width σ_α may also be developed for quadratic potentials.[19] Non-Born-Oppenheimer semiclassical trajectories, in general, represent a system in a superposition of electronic states. One may assign p_α for each state α at any instant along a non-Born-Oppenheimer trajectory to be equal to the nuclear momentum that the trajectory would have if it existed in the pure state α. (Special consideration is required for energetically closed electronic states, but we do not consider this complication here.) Assigning values for x_α and σ_α is not straightforward for non-Born-Oppenheimer trajectories. For example, if one sets x_α for all α equal to the same value (say, the position of the semiclassical trajectory), one loses the first term in Eq. (7). By using the principles pre-

sented in the Introduction and a reasonable set of assumptions, we will develop expressions for the parameters x_α and σ_α.

Next, we assume that the widths of the wave packets are independent of electronic state, and we set $\sigma_\alpha^2 = s$. This reduces Eq. (7) to

$$k_{\alpha\beta} = \frac{(x_\alpha - x_\beta)(p_\alpha - p_\beta)}{4ms} + \frac{s(p_\alpha - p_\beta)(F_\alpha - F_\beta)}{\hbar^2}. \quad (8)$$

The two terms in Eq. (8) reflect two aspects of the decay of the overlap: separation of the coordinate centers of states α and β and dispersion of the nuclear momentum for states α and β. The relative importance of these contributions is controlled by the width parameter s. When s is large (corresponding to packets delocalized in x and localized in p), the decay rate becomes large and is dominated by the instantaneous separation of the centers of the wave packets. When s is small (corresponding to localization in x and delocalization in p), the rate of decoherence is dominated by the dispersion of the nuclear momenta. In the limits of $s=0$ or ∞, the decay rate is infinite, independent of the positions and momenta of the wave packets. For intermediate cases, both decay mechanisms are expected to be important.

To obtain a useful formula from Eq. (8), prescriptions for x_α, p_α, F_α, and s need to be specified. The initial separation of the centers of the wave packets in coordinate space $D_{\alpha\beta} = x_\alpha - x_\beta$ defines a choice of basis functions with which to represent electronic decoherence semiclassically, and $D_{\alpha\beta}$ is determined by optimizing the basis, which, according to the second principle from the Introduction, corresponds to maximizing the decay rate with respect to $D_{\alpha\beta}$.

We consider a two-state case where $p_\beta < p_\alpha$ and $x_\beta < x_\alpha$. Optimizing $\dot{O}_{\alpha\beta}$ with respect to $D_{\alpha\beta}$ gives

$$\frac{(p_\alpha - p_\beta)}{16ms^2}D_{\alpha\beta}^2 + \frac{(p_\alpha - p_\beta)(F_\alpha - F_\beta)}{4\hbar^2}D_{\alpha\beta} - \frac{(p_\alpha - p_\beta)}{4ms} = 0, \quad (9)$$

whose solutions are (for $p_\alpha \neq p_\beta$)

$$D_\pm = -2(F_\alpha - F_\beta)ms^2/\hbar^2 \pm 2\sqrt{s + (F_\alpha - F_\beta)^2 m^2 s^4/\hbar^4}. \quad (10)$$

Note that because $s > 0$, the magnitude of the second term is always greater than the magnitude of the first term, making $D_+ > 0$ and $D_- < 0$ for all possible values of the parameters. We choose the solution where the packet on the lower electronic state (state α in our example) is advanced in coordinate space relative to the packet on the other electronic state, i.e., we choose D_+ as our solution, giving [using Eq. (8)]

$$k_{\alpha\beta} = \frac{s(p_\alpha - p_\beta)(F_\alpha - F_\beta)}{2\hbar^2}$$
$$+ \sqrt{\frac{(p_\alpha - p_\beta)^2}{4m^2s} + \frac{(p_\alpha - p_\beta)^2(F_\alpha - F_\beta)^2 s^2}{4\hbar^2}}. \quad (11)$$

The first term may be either positive or negative, and its sign depends on the sign of $(F_\alpha - F_\beta)$. The overall rate constant, however, is always non-negative.

Using the minimum-uncertainty relationship for the uncertainties in x and p, one can write

$$s = \frac{\hbar}{2} \frac{\Delta x}{\Delta p}. \quad (12)$$

We approximate the ratio $\Delta x / \Delta p$ as the ratio of the de Broglie wavelength for the average momentum $\bar{p}$ to the momentum difference, i.e.,

$$s = \frac{\hbar}{2} \frac{h/\bar{p}}{|p_\alpha - p_\beta|}, \quad (13)$$

where $\bar{p}$ is defined to be positive. Using the identity (which arises from the conservation of the sum of kinetic and potential energies)

$$|p_\alpha - p_\beta|\bar{p} = m|V_\alpha - V_\beta|, \quad (14)$$

where V_α is the potential energy of electronic state α, the width may be written as

$$s = \frac{\hbar^2 \pi}{m|V_\alpha - V_\beta|}. \quad (15)$$

The rate constant for this choice of the width is

$$k_{\alpha\beta} = \frac{\pi}{2} \frac{(F_\alpha - F_\beta)}{\bar{p}}$$
$$+ \sqrt{\frac{(p_\alpha - p_\beta)^2|V_\alpha - V_\beta|}{4m\hbar^2\pi^2} + \frac{\pi^2}{4}\frac{(F_\alpha - F_\beta)^2}{\bar{p}^2}}. \quad (16)$$

Finally, we assume that p_α, F_α, and V_α are readily obtained from the particulars of the problem being modeled, and Eq. (16) is the major result of this paper.

Writing Eq. (16) as

$$k_{\alpha\beta} = k_{\alpha\beta}^{\Delta F} + \sqrt{(k_{\alpha\beta}^{\Delta p})^2 + (k_{\alpha\beta}^{\Delta F})^2}, \quad (17)$$

one may identify the decay as arising from terms involving the difference in forces and the difference in momenta.

We have previously developed models for introducing decoherence in non-Born-Oppenheimer trajectories[14–16,20] using the following expression for the decay time $\tau_{\alpha\beta}$ ($\tau_{\alpha\beta} \equiv k_{\alpha\beta}^{-1}$)

$$\tau_{\alpha\beta} = \frac{\hbar}{|V_\alpha - V_\beta|}\left(1 + \frac{E_0}{T_{nuc}}\right). \quad (18)$$

where E_0 is a parameter and T_{nuc} is the nuclear kinetic energy. In the limit of parallel surfaces, the entire decay rate arises from the terms involving the difference in momenta, and the decay time of Eq. (17) may be written in this limit as

$$\tau_{\alpha\beta}^{\Delta p} = \frac{2\pi\hbar}{|V_\alpha - V_\beta|}\sqrt{\frac{\bar{p}}{|p_\alpha - p_\beta|}}. \quad (19)$$

For small p_β (such that $\bar{p} \approx p_\alpha/2$), Eqs. (18) and (19) are equal for $E_0 = (\sqrt{2}\pi - 1)T_{nuc} \approx 3.4T_{nuc}$. This is in qualitative agreement with our previously recommended value of $E_0 = 0.1E_h = 2.7$ eV, which was empirically optimized[16] for several realistic model systems with kinetic energies on the order of 1 eV.

Rossky and co-workers[12,13,17] obtained good results for the systems they studied by extracting a first-order rate constant equal to (in one dimension)

$$\tau_{\alpha\beta} = \frac{\hbar}{\sigma_{\alpha\beta}(F_\alpha - F_\beta)}. \tag{20}$$

In applications of Eq. (20), a thermal average for the width was appropriate, and the one used is equivalent to

$$\sigma_{\alpha\beta} = \frac{\hbar}{\sqrt{12mkT}}, \tag{21}$$

where T is the temperature. To make comparisons with the other formulas discussed here (which do not incorporate thermal averaging) more straightforward, we write $p_0 = \sqrt{2mkT}$ as a parameter and rewrite Eq. (20) [with the width of Eq. (21)] as

$$\tau_{\alpha\beta} = \frac{\sqrt{6}p_0}{F_\alpha - F_\beta}. \tag{22}$$

The result in Eq. (22) is approximately equal to that of Eq. (16) in the limit where $p = p_\alpha = p_\beta$ for $p_0 = \sim 0.1p$.

III. CONCLUSIONS

An expression for the decay rate of the reduced electronic density matrix has been derived by analyzing the behavior of minimum-uncertainty wave packets and by optimizing parameters of the basis with respect to the decay rate. The resulting formula [Eq. (16)] is obtained in first order, may be used for nonthermal systems, and involves quantities readily computable from semiclassical molecular-dynamics calculations. The formula was shown to have a reasonable magnitude and functional form and is inclusive of two other previously proposed and successfully applied formulas.

The formula presented here for the decay time is directly applicable in semiclassical electronically nonadiabatic theories that include decoherence.[7–9,13–16,21–30] Similar analyses may be useful in other contexts as well, for example[31–35] where a single nuclear coordinate or vibrational mode is treated quantum mechanically with other nuclear degrees of freedom treated classically.

[1] B. L. Hu, J. B. Paz, and Y. Zhang, Phys. Rev. D **45**, 2843 (1992).
[2] J. B. Paz and S. Sinha, Phys. Rev. D **44**, 1038 (1991).
[3] J. B. Paz, S. Habib, and W. H. Zurek, Phys. Rev. D **47**, 488 (1993).
[4] M. Simonius, Phys. Rev. Lett. **40**, 980 (1978).
[5] W. H. Zurek, Phys. Rev. D **26**, 1862 (1982).
[6] R. Kosloff, M. A. Ratner, and W. B. Davis, J. Chem. Phys. **106**, 7036 (1997).
[7] V. May and O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems* (Wiley-VCH, Berlin, 2000).
[8] A. V. Pisliakov, M. F. Gelin, and W. Domcke, J. Phys. Chem. A **107**, 2657 (2003).
[9] V. Mujica and M. A. Ratner, in *Handbook of Nanoscience, Engineering and Technology*, edited by W. A. Goddard, D. W. Brenner, S. E. Lyshevski, and G. J. Iafrate (CRC, Boca Raton, Florida, 2003), Chap. 10.
[10] X.-Y. Zhu, Surf. Sci. Rep. **56**, 1 (2004).
[11] M. Kleckner and A. Ron, Phys. Rev. A **63**, 022110 (2001).
[12] O. Prezhdo and P. J. Rossky, J. Chem. Phys. **107**, 5863 (1997).
[13] L. Turi and P. J. Rossky, J. Chem. Phys. **120**, 3688 (2004).
[14] M. D. Hack and D. G. Truhlar, J. Chem. Phys. **114**, 9305 (2001).
[15] C. Zhu, S. Nangia, A. W. Jasper, and D. G. Truhlar, J. Chem. Phys. **121**, 7658 (2004).
[16] C. Zhu, A. W. Jasper, and D. G. Truhlar, J. Chem. Phys. **120**, 5543 (2004).
[17] H. Hwang and P. J. Rossky, J. Phys. Chem. B **108**, 6723 (2004).
[18] G. A. Fiete and E. J. Heller, Phys. Rev. A **68**, 022112 (2003).
[19] E. J. Heller, J. Chem. Phys. **62**, 1544 (1975).
[20] A. W. Jasper, S. Nangia, C. Zhu, and D. G. Truhlar, Acc. Chem. Res. (accepted).
[21] J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).
[22] J. C. Tully, in *Modern Methods for Multidimensional Dynamics Computations in Chemistry*, edited by D. L. Thompson (World Scientific, Singapore, 1998), pp. 34–72.
[23] S. Adhikari and G. D. Billing, J. Chem. Phys. **111**, 48 (1999).
[24] K. F. Wong and P. J. Rossky, J. Chem. Phys. **116**, 8418 (2002).
[25] K. F. Wong and P. J. Rossky, J. Chem. Phys. **116**, 8429 (2002).
[26] D. A. Micha and B. Thorndyke, Int. J. Quantum Chem. **90**, 759 (2002).
[27] I. Horenko, C. Salzmann, B. Schmidt, and C. Schütte, J. Chem. Phys. **117**, 11075 (2002).
[28] J. Gong and P. Brumer, Phys. Rev. A **68**, 022101 (2003).
[29] B. Thorndyke and D. A. Micha, Chem. Phys. Lett. **403**, 280 (2005).
[30] I. Burghardt, J. Chem. Phys. **122**, 94103 (2005).
[31] J. W. Duff and D. G. Truhlar, J. Chem. Phys. **63**, 4418 (1975).
[32] W. R. Gentry, in *Atom-Molecule Collision Theory*, edited by R. B. Bernstein (Plenum, New York, 1979), p. 391.
[33] L. L. Halcomb and D. J. Diestler, J. Chem. Phys. **121**, 3393 (2004).
[34] G. D. Billing, Int. Rev. Phys. Chem. **13**, 309 (1994).
[35] Q. Shi and E. Geva, J. Chem. Phys. **121**, 3393 (2004).